Attempts to Synthesize Cyclic Group 8 Metallaesters

Thesis by

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ABSTRACT

In studying a proposed carbon monoxide reduction scheme an attempt has been made to synthesize bifunctional group 8 transition metal carbonyl complexes containing intramolecular nucleophiles. The incorporation of alkoxide nucleophiles through cyclopentadienyl ligands was hoped to encourage attack on carbonyl ligands thereby forming cyclic metallaesters. The attempts to synthesize these substituted cyclopentadienyl group 8 transition metal complexes have thus far been unsuccessful.

INTRODUCTION

For several years the attention of the world has been directed to the possibility that the current supply of natural resources may soon be depleted to the point where significant changes in their present methods of use will become necessary. One extremely important concern is the availability of fuels and chemical feedstocks. Currently both of these demands are supplied primarily through the petroleum industry. Recently the desire for energy independence along with the threat of dwindling petroleum supplies has prompted consideration of other fuel sources. In countries where large coal deposits are found the possibility of producing fuel from coal is found in heterogeneous reduction of carbon monoxide by hydrogen through the Fischer-Tropsch process (Eq. 3) (*1*).

PARTIAL COMBUSTION:

$$\text{COAL} \longrightarrow CO + H_2 \qquad (1)$$

WATER-GAS SHIFT REACTION:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2)$$

FISCHER-TROPSCH PROCESS:

$$CO + H_2 \longrightarrow \text{ORGANIC PRODUCTS} \qquad (3)$$

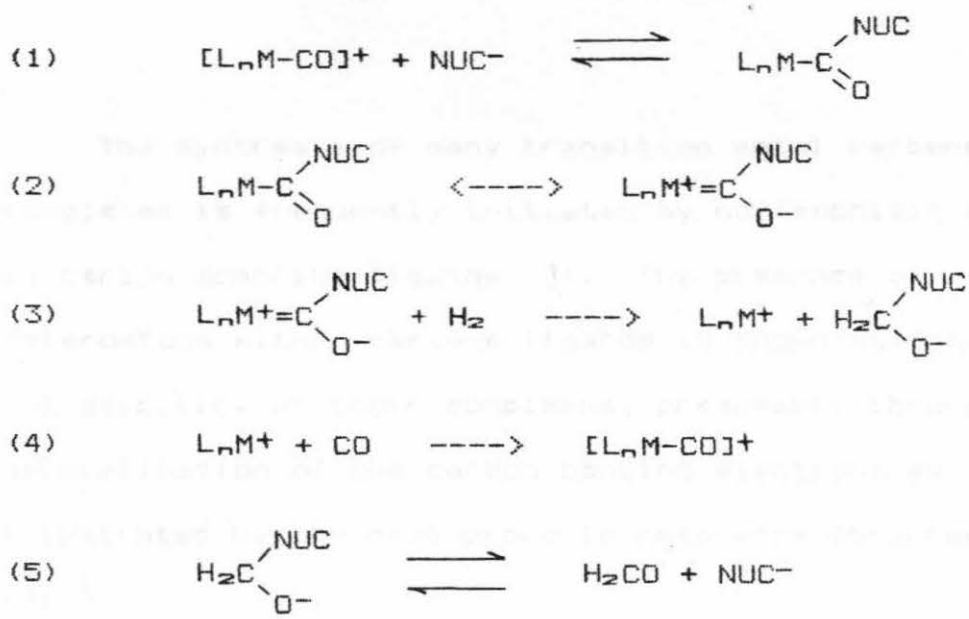
The partial combustion of coal in the presence of steam gives a gaseous mixture of carbon monoxide and hydrogen (Eq. 1). Frequently this mixture is not rich enough in hydrogen to be used efficiently in the Fischer-Tropsch process. The $CO:H_2$ ratio can be adjusted to an optimum value through the water-gas shift reaction (Eq. 2). The Fischer-Tropsch process can then be used to convert carbon monoxide to a variety of organic products. Often this process is plagued by limited selectivity. A mixture of straight chain hydrocarbons, alcohols, aldehydes, and carboxylic acids is obtained. There would be a clear economic advantage in acquiring the ability to control carbon monoxide reduction products to a greater degree. However, since the Fischer-Tropsch process is heterogeneously catalyzed the mechanism is difficult to study and is not yet well understood (*1*).

The research to be described in this report involves the investigation of a scheme which is designed to homogeneously reduce carbon monoxide. In this sense the system models the Fischer-Tropsch process. It is hoped that the use of a homogeneous system will allow synthesis and isolation of chemical species which are intermediates in carbon monoxide reduction. Understanding these intermediates will assist in the development of more selective reduction processes (*1d*).

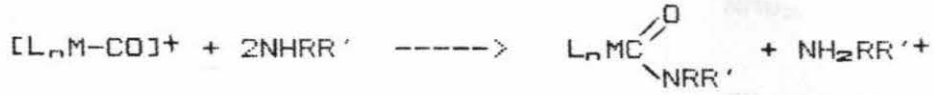
The proposed scheme is presented in Scheme 1. The

initial step is nucleophilic attack on a carbonyl ligand of a cationic transition metal carbonyl complex. The product of this reaction can be represented by the two resonance structures shown in step 2. The right hand resonance structure depicts the complex as a zwitterionic carbene. The following steps involve hydrogenation of this carbene, addition of carbon monoxide to the unsaturated metal center, release of the nucleophile from the reduced carbon monoxide product, and coupling of carbon fragments.

SCHEME 1:



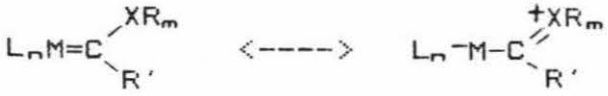
The reaction of a nucleophile and a transition metal carbonyl to form an acyl product (step 1) has been known for some time. Specifically, Angelici has found that transition metal complexes with carbonyl ligands which have infrared absorptions at greater than 2000cm^{-1} will react with amine or alkoxide nucleophiles to form amide or ester complexes, respectively (Eq. 4, 5) (2).



(4)

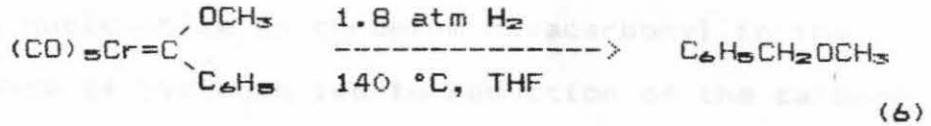
(5)

The synthesis of many transition metal carbene complexes is frequently initiated by nucleophilic attack on carbon monoxide ligands (3). The presence of heteroatoms within carbene ligands is known to enhance the stability of their complexes, presumably through delocalization of the carbon bonding electrons as illustrated by the most probable resonance structures (4).



X = N, O, etc.

The reduction of transition metal carbene complexes by hydrogen has been observed in several cases (Eq. 6, 7) (5-7).



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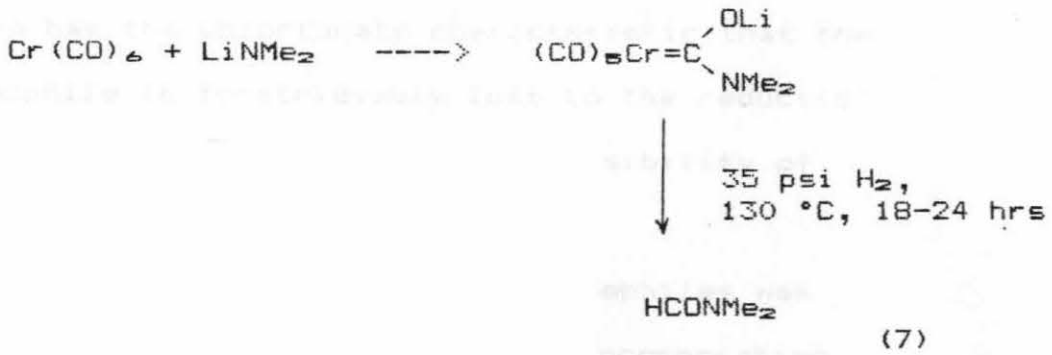


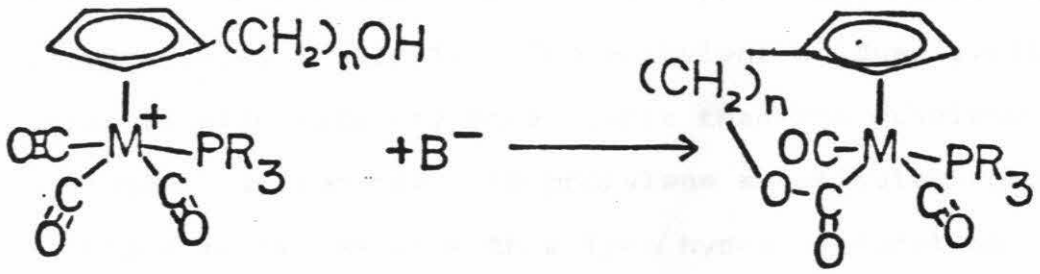
(7)

The inclusion of steps 4-6 completes this proposed catalytic cycle to give a scheme which is feasible according to our present knowledge of organo-transition metal chemistry.

RESULTS AND DISCUSSION

The initial efforts toward developing a system which might act as indicated in Scheme 1 are reflected in equation 7 above. In this case the attack of an amide nucleophile on chromium hexacarbonyl in the presence of hydrogen led to reduction of the carbene intermediate to dimethyl formamide (7). However, this system has the unfortunate characteristic that the nucleophile is irretrievably lost to the reduction product, thereby eliminating the possibility of establishing a catalytic cycle.

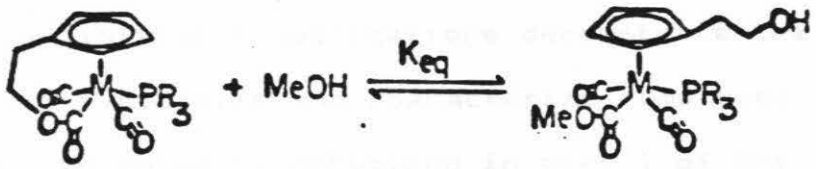
The use of intramolecular nucleophiles was considered as a possible method of incorporating retrievable nucleophiles into the system. A series of cyclic metallaesters was synthesized from group 6 transition metal carbonyl cyclopentadienyl cations (Eq. 8) (8). The cyclopentadienyl ring was substituted with an alcohol. Treatment of the cation with sodium methoxide deprotonates the alcohol functionality and produces an alkoxide nucleophile. Intramolecular nucleophilic attack on a carbonyl ligand then forms the metallaester.



(8)

M = Mo, W; n = 1, 2, 3; R = phenyl, p-tolyl (Ref.8)

An important variable in the formation of these intramolecular esters is the length of the carbon chain connecting the cyclopentadienyl ring and the ester group. The determination of the methanolysis equilibria of the cyclic metallaesters illustrates the effect of changing arm length (Eq. 9).



(9)

(Ref. 8)

Cyclic ester formation is strongly favored over methyl ester formation for the methylene and ethylene bridged cases (Table 1). The methylene bridged cyclic ester is significantly more stable than the ethylene analogue. In contrast the propylene substituted complex favors a methyl ester with a free hydroxyl function rather than the cyclic ester.

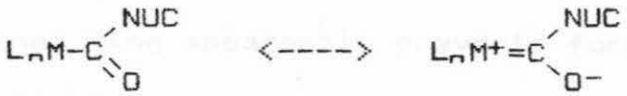
TABLE 1. Intra Versus Intermolecular Ester Equilibrium Constants (Eq. 9) (Ref. 8) .

METAL	R	CARBON BRIDGE LENGTH	K_{eq}(M^{-1}, 25 °C)
W	phenyl	1	4.2(8)
Mo	p-tolyl	2	17(3)
W	p-tolyl	2	40(12)
Mo	phenyl	3	230(40)
W	phenyl	3	117(19)

These initial investigations demonstrate the ability to synthesize and characterize complexes analogous to those hypothesized in step 1 of the proposed carbon monoxide reduction scheme. The extent to which the carbonyl cations will undergo this esterification reaction can be optimized by adjusting the arm length which delivers the alkoxide nucleophile. In addition the nucleophile has been incorporated into

the metal complex so that it is more likely to remain active in subsequent reactions.

A series of reactions were performed in order to investigate the extent to which the carbene resonance form of step 2 describes the cyclic metallaesters.



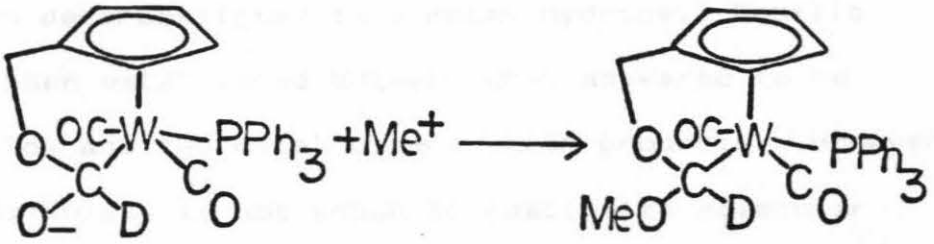
The first reaction attempted was the reaction with carbon monoxide and hydrogen in the hope that the esters would act as carbon monoxide reduction catalysts. However this lead only to decomposition of the metallaesters.

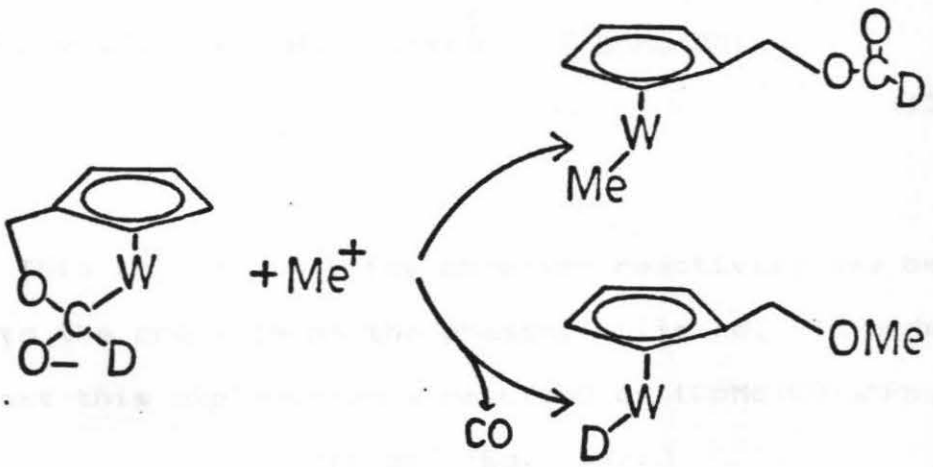
Reaction with alkylating agents was expected to give a bisalkoxy carbene complex (5), but lead only to a de-esterification in which the alkoxide nucleophile was converted into an ether (Eq. 10).

(10)

(Ref. 8)

In contrast to the above reactions, the reaction with hydride reagents gave the expected attack at the electrophilic carbene carbon (5) to form a hemiacetal anion. In the case of the methylene bridged arm alkylation of the hemiacetal ion gave an acetal. Side reactions involving the ring opening of the cyclic ester were also observed. In the ethylene bridged case the easily opened ring apparently prevents formation of a cyclic hemiacetal.





(Ref. 8)

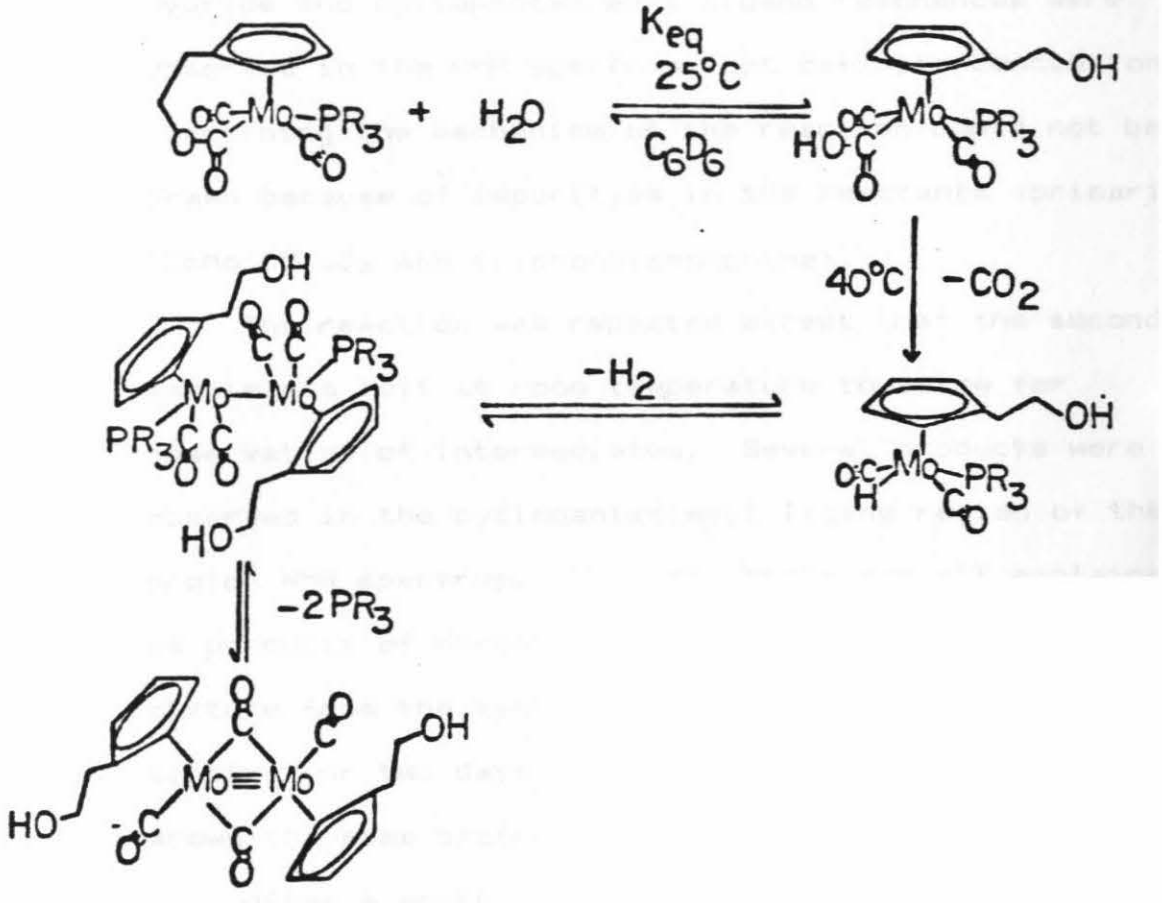
The identification of the hydride reduction products is based on comparison of the observed deuterium or proton NMR resonances to those reported for other transition metal hemiacetal or acetal complexes (9). Several attempts were made to isolate the hemiacetal products but this has not yet been successful.

The final reaction which was investigated was that of the molybdenum metallaesters with water (scheme 2). This resulted in formation of a metallacarboxylic acid which decarboxylated to a metal hydride. Equilibrium was then established between what appeared to be the hydride and two metal dimerization products. However, $[CpMo(CO)_3]_2$ is not known to react with molecular hydrogen under similar conditions (Eq. 13) (*10*).

$$[CpMo(CO)_3]_2 \quad + \quad H_2 \quad \text{--X-->} \quad 2\ CpMo(CO)_3H \qquad (13)$$

This implies that the observed reactivity may be due to the presence of the phosphine ligand. In order to test this explanation a reaction of $[CpMo(CO)_2PPh_3]_2$ with hydrogen was performed (Eq. 14).

SCHEME 2: Ref. 8



$$[CpMo(CO)_2PPh_3]_2 + H_2 \xrightarrow{?} CpMo(CO)_2PPh_3H \quad (14)$$

After heating to 40 °C for 24 hours and then sitting at room temperature for one month the expected hydride and cyclopentadienyl ligand resonances were observed in the NMR spectrum, but definite conclusions concerning the mechanism of the reaction could not be drawn because of impurities in the reactants (primarily $[CpMo(CO)_2]_2$ and triphenylphosphine).

The reaction was repeated except that the second sample was left at room temperature to allow for observation of intermediates. Several products were observed in the cyclopentadienyl ligand region of the proton NMR spectrum. However, these are all explained as products of decomposition reactions. The reaction mixture from the synthesis of $[CpMo(CO)_2PPh_3]_2$, after sitting for two days, without contact with hydrogen, shows the same proton resonances.

After a month, since no hydride formation had been observed at room temperature, the sample was heated to 40 °C for approximately a week. At this point an anomolous observation was made during acquisition of the NMR spectra. The sample solution was light pink when it was placed in the room temperature probe of the NMR

spectrometer. After the spectrum was obtained it was noted that the sample had turned yellow. Upon sitting at room temperature the solution returned to its previous pink color. In obtaining another spectrum the color change was observed again, but upon sitting out of the NMR spectrometer probe the color always returned to pink. Later the color remained pink regardless of whether it was placed in the NMR probe or not.

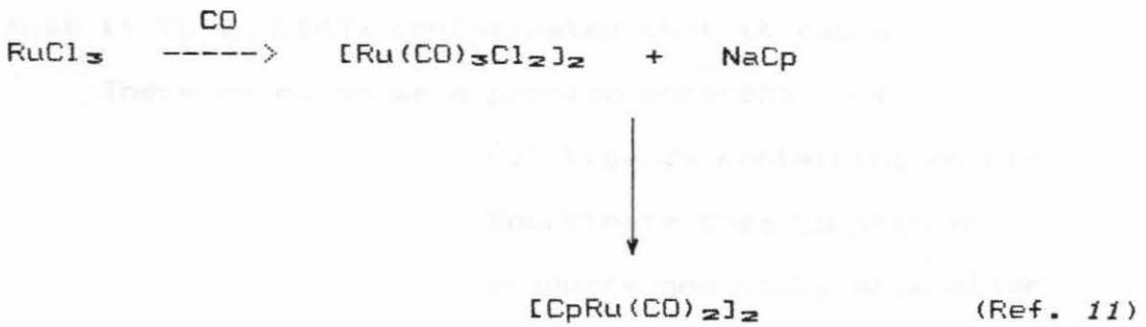
The sample was then kept at room temperature for an additional three weeks. Unfortunately, even after two months total reaction time no observable $CpMo(CO)_2PPh_3H$ had been formed.

In the experiments described above a major problem was the low solubility of $[CpMo(CO)_2PPh_3]_2$. The inability to obtain concentrated samples prevented the acquisition of phosphorus NMR spectra with good signal to noise ratios. This is also the reason for the difficulty in obtaining a pure sample, since the dimer falls out of solution during its synthesis and occludes impurities which are removed with great difficulty if at all. In an attempt to increase the solubility of the dimer without greatly altering its reactivity, tri-p-tolylphosphine was substituted for triphenyl-phosphine. However, the same difficulty was experienced and no benefit was found in this change.

The group 6 metal complexes described above were studied because of their synthetic accessibility.

However, most of the known Fischer-Tropsch catalysts are based on metals within groups 8-10 (*1*). Also, although several carbene complexes have been subjected to reducing conditions, the general observation has been that the group 6 transition metal carbenes either decompose or undergo no reaction (5). Notice that the chromium systems mentioned in the introduction (eq. 6, 7) are exceptions to this rule. Several group 8 transition metal carbene complexes are known to undergo clean reductions with either molecular hydrogen or hydride (5). Therefore it is reasonable to expect that group 8 based systems will give additional insight into the requirements for design of a carbon monoxide reduction system such as that outlined in scheme 1.

It was hoped that ruthenium or iron carbonyl cationic complexes containing substituted cyclopentadienyl ligands could be synthesized through known routes to the plain ring complexes.



$$Fe(CO)_5 + C_5H_6 \longrightarrow [CpFe(CO)_2]_2$$

(Ref. *18*)

$$[CpFe(CO)_2]_2 + I_2 \longrightarrow CpFe(CO)_2I$$

$$CpFe(CO)_2I + AgBF_4 + PR_3 \longrightarrow [CpFe(CO)_2PR_3]BF_4$$

(Ref. *12*)

The infrared carbonyl stretching frequencies of these plain ring cationic complexes indicate that they should undergo nucleophilic attack. Therefore the incorporation of an intramolecular nucleophile is expected to allow formation of cyclic metallaesters analagous to the molybdenum and tungsten complexes discussed earlier (*13*, *14*).

However, the initial coordination of the substituted cyclopentadienyl ligand to iron or ruthenium centers has been a major obstacle. Several approaches have been attempted but in each case it has been found that either none of the desired product is obtained or that it is so badly contaminated that it cannot be used.

There seems to be a problem inherent in the use of substituted cyclopentadienyl ligands containing oxygen atoms when attempting to coordinate them to iron or ruthenium. The reaction products generally show major impurities in the proton NMR spectrum ranging from 1.5 to 3.0 ppm. These have not been identified but may

indicate destruction of the cyclopentadienyl ligand rather than coordination. Also, it was not uncommon to obtain a large amount of insoluble material as a result of these reactions, perhaps due to formation of metal oxides or clusters.

The first attempt towards coordinating a substituted cyclopentadienyl ring to an iron center involved the use of 2-hydroxyethylcyclopentadiene and $Fe(CO)_5$. The two reactants were refluxed in THF but only decomposition occured (Eq. 17).

$$Fe(CO)_5 + Cp(H)(CH_2CH_2OH) \xrightarrow{X} [(\eta^5\text{-}CpEtOH)Fe(CO)_2]_2 \quad (17)$$

Because of the difficulty of synthesizing the ethanol substituted cyclopentadiene ligand and the advantage of the single carbon chain in forming cyclic metallaesters, the precursor to methanol substituted cyclopentadienyl complexes (sodium formyl-cyclopentadienide) was employed in the following experiments.

Shvo has shown that the treatment of iron pentacarbonyl with trimethylamine oxide allows dienes to easily coordinate to the iron center (*19*). It was hoped that the intermediate formed by oxidation of one of the carbonyl ligands (*20*) would allow coordination of the

substituted cyclopentadienyl ligand. This did not prove to be the case (Eq. 18).

$$Fe(CO)_5 + Me_3NO + Na[CpCHO] \text{ --X--> } Na[(\eta^5\text{-}CpCHO)Fe(CO)_2] \quad (18)$$

Because of the difficulties in obtaining substituted cyclopentadienyl iron carbonyl complexes, the synthesis of the analagous ruthenium complexes was attempted. $Na[(\eta^5\text{-}C_5H_4CHO)W(CO)_3]$ is easily obtained by refluxing a THF solution of sodium formyl cyclopentadienide and tungsten hexacarbonyl. However, the substitution of ruthenium carbonyl did not give the desired products (Eq. 19).

$$Ru_3(CO)_{12} + NaCpCHO \text{ --X--> } Na[(\eta^5\text{-}CpCHO)Ru(CO)_2] \quad (19)$$

Although $[CpRu(CO)_2]_2$ could be obtained from the reaction of NaCp with $[Ru(CO)_3Cl_2]_2$ the substituted ring complex could not be obtained in this way (Eq. 20).

$$NaCp + [Ru(CO)_3Cl_2]_2 \text{ -----> } [CpRu(CO)_2]_2$$

$$Na[CpCHO] + [Ru(CO)_3Cl_2]_2 \xrightarrow{X} [(\eta^5\text{-}CpCHO)Ru(CO)_2]_2 \quad (20)$$

Rausch has reported the synthesis of substituted cyclopentadienyl cobalt carbonyl complexes obtained through halogen intermediates from the reaction of iodine with cobalt carbonyl (Eq. 21) (*21*).

$$Co_2(CO)_8 + I_2 \longrightarrow [\text{iodo intermediate}] + Na[CpCHO] \longrightarrow (\eta^5\text{-}CpCHO)Co(CO)_2 \quad (21)$$

Unfortunately, this same strategy was not successful in the ruthenium case (Eq. 22).

$$Ru_3(CO)_{12} + I_2 + Na[CpCHO] \xrightarrow{X} [(\eta^5 CpCHO)Ru(CO)_2]_2 \quad (22)$$

The formyl functionality of the substituted cyclopentadienyl complex $Na[(\eta^5\text{-}C_5H_4CHO)W(CO)_3]$ is easily reduced to an alcohol by treatment with $NaBH_4$ in

ethanol solution (8). It was hoped that this reduction could be carried out before complexation to the metal center, and that this would avoid the synthetic problems described above. However, the sodium salt was not successfully reduced (eq. 23).

$$Na[CpCHO] + NaBH_4 \text{ --X--> } Na[CpCH_2OH] \qquad (23)$$

It is clear from this set of experiments that the extension of the principles first studied in the group 6 cyclic metallaesters into group 8 transition metal systems is not as straight forward as was hoped. The many unexpected problems in synthesizing substituted cyclopentadienyl iron or ruthenium carbonyl complexes has hindered progress for this entire project. If these problems are due to the reactivity of the oxygen atom on the substituted ligand then the use of iron or ruthenium systems may not be feasible.

It may be that the reduction to an alcohol of the formyl group of sodium formyl cyclopentadienide before attempting to complex this ligand to the transition metal may alleviate some of the difficulties, but this will require a stronger reducing agent than has been used at this time.

Another possibility involves the use of thallium

reagents. Perhaps thallium formylcyclopentadienide can be reduced to the alcohol substituted complex and then transfer the cyclopentadiene ring to iron or ruthenium. This exchange is known for the plain ring systems in the ruthenium case (Eq. 24) (24).

$$TlCp + [Ru(CO)_3Cl_2]_2 \longrightarrow [CpRu(CO)_2]_2 \qquad (24)$$

The possibility of employing cobalt or rhodium centered complexes is also interesting. The cobalt complex $(\eta^5\text{-}CpCHO)Co(CO)_2$ is reported to undergo reduction of the formyl group to give the alcohol substituted ring complex. The infrared spectrum of this complex indicates that deprotonation of the alcohol should lead to nucleophilic attack at one of the carbonyl ligands, but this has not yet been attempted. This would change the total charge on the expected metallaester, making it an anion. This might enhance the importance of the carbene resonance form (Eq. 25)

$$(\eta^5\text{-}CpCH_2OH)Co(CO)_2 + {}^-OMe \xrightarrow{?} (CO)CpCo{=}C(O)(O^-) \qquad (25)$$

EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques on a dual manifold vacuum line under argon atmosphere. Argon was purified before use by passage through columns of BASF RS-11 (Chemalog) and Linde 4A molecular sieves. Long term storage of transition metal complexes and some manipulations were carried out in a Vacuum Atmospheres dry box under nitrogen atmosphere. Tetrahydrofuran, toluene, pentane, and ethyl ether were vacuum transferred from sodium benzophenone ketyl prior to use. Dichloromethane was vacuum transferred from phosphorus pentoxide. Acetonitrile and acetone were dried over molecular sieves and degasses prior to use. Triphenylphosphine was purchased from Aldrich and tri-p-tolylphosphine was purchased from Strem. Both were recrystallized from ethanol prior to use. $RuCl_3 \cdot xH_2O$ was purchased from Strem. NMR spectra were obtained on Jeol FX-900 or Varian EM390 spectrometers. Infrared spectra were obtained on a Shimadzu IR-435 spectrophotometer.

Cyclic tungsten metallaesters (*8b*) and $[CpFe(CO)_2PPh_3]BF_4$ (*12*) were prepared by literature methods.

The preparation of $[CpMo(CO)_2]_2$and $[CpMo(CO)_2PPh_3]_2$ followed literature methods (*16*) with the change to tetrahydrofuran solvent for the preparation of the

latter.

The reaction of $[CpMo(CO)_2PPh_3]_2$ with H_2 and the reduction of tungsten metallaesters followed the procedure of Coolbaugh (*8b*).

Preparation of $Na[C_5H_4CHO]$. The method of Rausch was employed (*21*). Sodium cyclopentadienide (1.24 g, 14.1 mmol) was placed under argon and dissolved in THF. Ethyl formate (1.30 mL, 15.5 mmol) was added and the mixture was refluxed for three hours. The mixture was allowed to cool and solvent was removed under reduced pressure. The resulting tan powder was extracted with acetonitrile. The acetonitrile solution was reduced in volume under reduced pressure and diethyl ether was added to give a light tan product whose proton NMR spectrum was in agreement with the literature. The product is very hygroscopic.

Attempted reduction of $Na[C_5H_4CHO]$. An ethanol solution of $Na[C_5H_4CHO]$ (0.09 g, 0.8 mmol) and $NaBH_4$ (0.02 g, 0.5 mmol) was stirred and heated to 60 °C for four hours. Diethyl ether was added to give a white precipitate of the starting material.

Preparation of $Na[(\eta^5-C_5H_4CHO)W(CO)_3]$. $W(CH_3CN)_3(CO)_3$ (5.5 g, 14 mmol) and Na[CpCHO] (1.95 g, 16.8 mmol) were dissolved in THF and then refluxed for five hours giving a dark red solution. Solvent was removed under reduced pressure and the resulting residue was recrystallized from THF/diethyl ether. Proton NMR

analysis of the product was in agreement with the literature (8).

Note: The use of acetonitrile as a solvent for recrystallization of $Na[C_5H_4CHO]$ or $Na[(\eta^5\text{-}C_5H_4CHO)W(CO)_3]$ is quite helpful but all acetonitrile must be completely removed by washing with diethyl ether before further reactions are attempted in order to avoid contaminating side reactions.

Attempted synthesis of $[(\eta^5\text{-}C_5H_4CH_2CH_2OH)Fe(CO)_2]_2$. The preparation of 2-hydroxyethylcyclopentadiene followed the literature method (8). Iron pentacarbonyl (0.80 g, 4.1 mmol) and 2-hydroxyethylcyclopentadiene (0.47 g, 4.4 mmol) were refluxed in tetrahydrofuran for twelve hours (18). A large amount of insoluble red-brown solid was obtained. Solvent was removed under reduced pressure and the resulting solid was extracted with dichloromethane. Proton NMR analysis did not show the characteristic resonances expected for the substituted cyclopentadienyl ligand.

Attempted synthesis of $Na[(\eta^5\text{-}C_5H_4CHO)Fe(CO)_2]$. The strategy of Shvo and Hazum (19) for synthesizing iron diene complexes using trimethyl amine oxide was employed. A benzene slurry of Me_3NO (2.3 g, 31 mmol) and Na[CpCHO] (1.28 g, 11 mmol) was stirred and cooled to 0 °C. $Fe(CO)_5$ (1.34 mL, 10 mmol) was syringed into the slurry. After gas evolution subsided the mixture

was refluxed for one hour and then cooled. A large amount of insoluble residue was obtained. The mixture was filtered and the remaining solid was washed with tetrahydrofuran. The filtrate and washes were combined and solvent was removed under reduced pressure. Proton NMR analysis of the resulting oil in $CDCl_3$ shows dominant resonances between 0.75 ppm and 2.50 ppm and only small resonances in the area where the cyclopentadienyl ligand protons are expected. No formyl proton resonances were observed.

Preparation of $[Ru(CO)_3Cl_2]_2$. The method of Gibson was used (22). $RuCl_3 \cdot xH_2O$ (2 g), concentrated HCl (15 mL), and 90% formic acid (20 mL) were refluxed for 3 days during which the solution went through several color changes (red, light brown, green, yellow). The solution was transferred to a beaker, and water was evaporated on a steam bath giving a yellow solid. This solid was used without further purification.

Reaction of $[Ru(CO)_3Cl_2]_2$ with NaCp. NaCp (0.1 g, 1.1 mmol) was dissolved in 20 mL THF. $[Ru(CO)_3Cl_2]_2$ (0.38 g, 0.7 mmol) was dissolved in 30 mL THF. The NaCp solution was then added to the ruthenium solution at which time some gas evolution occurred. The mixture was refluxed for 24 hours. The yellow solution was cooled and solvent was removed under reduced pressure. The resulting yellow solid was extracted with benzene. Proton NMR showed three products containing

cyclopentadienyl ligands. These presumably are ruthenocene, $[CpRu(CO)_2]_2$, and $CpRu(CO)_2Cl$ (23, 24, 25).

Attempted preparation of (η^5-C_5H_4CHO) ruthenium dicarbonyl complexes.

A. $[Ru(CO)_3Cl_2]_2$ and Na[CpCHO] were reacted under the conditions described for the unsubstituted cyclopentadienyl ligand. However, after 30 min. the reaction mixture turned dark red. Proton NMR analysis of the products after removal of solvent showed resonances attributable to the desired products (formyl proton at 9.63 ppm, cyclopentadienyl protons at 5.85 ppm and 5.48 ppm) but the major peak is at 2.08 ppm and is unidentified. Attempts to purify the reaction mixture were unsuccessful. Attempts to optimize reaction conditions by purification of starting materials or by reacting at room temperature failed to give the desired products.

B. Based on the synthesis of Na[(η^5-C_5H_4CHO)$W(CO)_3$] from $W(CO)_6$ and Na[CpCHO], $Ru_3(CO)_{12}$ and Na[CpCHO] were refluxed in THF. The mixture rapidly became red as in part A. above. The mixture was cooled and solvent was removed under reduced pressure. Proton NMR analysis did not reveal any of the desired product.

C. Based on the synthesis of (η^5-C_5H_4CHO)$Co(CO)_2$ (21) $Ru_3(CO)_{12}$ and one equivalent of I_2 were dissolved in THF and stirred for two hours. One equivalent of Na[CpCHO] was then added at which time the mixture turned dark

red. None of the desired product was obtained.

REFERENCES

(1) a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103. b) Biloen, P.; Sachtler, W.M.H. *Adv. Catalysis* **1981**, *30*, 165-216. c) Rofer-DePoorter, C.K. *Chem. Rev.* **1981**, *81*, 447-474. d) Herrmann, W.A. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 117-130.

(2) Angelici, R.J. *Accts. Chem. Res.* **1972**, *5*, 335-341.

(3) a) Cardin, D.J.; Cetinkaya, B.; Lappert, M.F. *Chem. Rev.* **1972**, *72*, 545-574. b) Cotton, F.A.; Lukehart, C.M. *Prog. Inorg. Chem.* **1972**, *16*, 487-613.

(4) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261-286.

(5) Brown, F.J. *Prog. Inorg. Chem.* **1980**, *27*, 1-122.

(6) Casey, C.P.; Neumann, S.M. *J. Am. Chem. Soc.* **1977**, *99*, 1651-1652.

(7) Doxsee, K.M.; Grubbs, R.H. *J. Am. Chem. Soc.* **1981**, *103*, 7696-7698.

(8) a) Coolbaugh, T.S.; Santarsiero, B.D.; Grubbs, R.H. *J. Am. Chem. Soc.* **1984**, *106*, 6310-6318. b) Coolbaugh, T.S., *Ph.D. Thesis, California Institute of Technology* **1985.**

(9) Casey, C.P.; Tukada, H.; Miles, W.H. *Organometallics* **1982**, *1*, 1083-1084.

(10) Bergman, R.G. *personal communication.*

(11) a) Bruce, M.I.; Stone, F.G.A. *J. Chem. Soc. (A)* **1967**, 1238. b) Blackmore, T.; Bruce, M.I.; Stone, F.G.A. *J. Chem. Soc. (A)* **1968**, 2158.

(12) Reger, D.L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153-162.

(13) Treichel, P.M.; Shubkin, R.L.; Barnett, K.W.; Reichard, D. *Inorganic Chem.* **1966**, *5*, 1177-1181.

(14) Kruse, A.E.; Angelici, R.J. *J. Organomet. Chem.* **1970**, *24*, 231-239.

(15) Caswell, M.; Schmir, G.L. *J. Am. Chem. Soc.* **1980**, *102*, 4815-4821.

(16) Curtis, M.D.; Klingler, R.J. *J. Organomet. Chem.* **1978**, *161*, 23-37.

(17) Solomons, T.W.G. *Organic Chemistry* **1980**, John Wiley & Sons, New York.

(18) King, R.B. *Organometallic Syntheses* **1965**, *1*, 114-115.

(19) Shvo, Y.; Hazum, E. *J. Chem. Soc. Chem. Commun.* **1975**, 829-830.

(20) Eekhof, J.H.; Hogeveen, H.; Kellogg, R.M. *J. Chem. Soc. Chem. Commun.* **1976**, 657.

(21) a) Hart, W.P.; Macomber, D.W.; Rausch, M.D. *J. Am. Chem. Soc.* **1980**, *102*, 1196-1198. b) Hart. W.P. *Ph.D. Thesis, University of Massachusetts* **1981**.

(22) Gibson, D.H.; Hsu, W.-L.; Steinmetz, A.L.; Johnson, B.V. *J. Organomet. Chem.* **1981**, *208*, 89-102.

(23) Haines, R.J.; du Preez, A.L. *J. Chem. Soc. Dalton* **1972**, 944-948.

(24) Wnuk, T.A.; Angelici, R.J. *Inorg. Chem.* **1977**, *16*, 1173-1179.

(25) Abrahamson, H.B.; Palazzotto, M.C.; Reichel, C.L.;

Wrighton, M.S. *J. Am. Chem. Soc.* **1979**, *101*, 4123-4127.